

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

WO 94/14990

(51) International Patent Classification 5 :
C22C 16/00, G21C 3/07

A1

(11) International Publication Number:

7 July 1994 (07.07.94)

(43) International Publication Date:

(31) International Application Number:

PCT/US93/07530

(22) International Filing Date:

12 August 1993 (12.08.93)

(30) Priority Data:
07/996,567

24 December 1992 (24.12.92) US

(71) Applicant: COMBUSTION ENGINEERING, INC. [US/US];
1000 Prospect Hill Road, P.O. Box 500, Windsor, CT 06095
(US).

(72) Inventors: GARDE, Anand, M.; 2 Sherwood Lane, West
Simsbury, CT 06092 (US). PATI, Sarya, R.; 5 Higate Lane,
Simsbury, CT 06070 (US).

(74) Agents: MULHOLLAND, John, H. et al.; ABB Combustion
Engineering Nuclear Power, Combustion Engineering, Inc.,
1000 Prospect Hill Road, P.O. Box 500, Windsor, CT 06095
(US).

(81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP,
KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, SK,
UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB,
GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ,
CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: ZIRCONIUM ALLOY WITH IMPROVED POST-IRRADIATION PROPERTIES

(57) Abstract

A stabilized alpha metal matrix provides an improved ductility, creep strength, and corrosion resistance against irradiation in a zirconium alloy containing tin in a range of 0.45 to 0.75 wt. %, and typically 0.6 wt. %; iron in a range of 0.4 to 0.53 wt. %, and typically 0.45 percent; chromium in a range of 0.2 to 0.3 wt. %, and typically 0.25 percent; niobium in a range of 0.3 to 0.5 wt. %, and typically 0.45 wt. %; nickel in a range of 0.012 to 0.03 wt. %, and typically 0.02 wt. %; silicon in a range of 50 to 200 ppm, and typically 100 ppm; and oxygen in a range 1000 to 2000 ppm, and typically 1600 ppm, with the balance zirconium. The addition of iron and niobium improves mechanical properties of the alloy with its lower level of tin, while corrosion resistance is addressed by having an iron level of 0.45 wt. % and an iron/chromium ratio on the order of 1.5. The addition of niobium also counters the effect of higher iron on the hydrogen absorption characteristics of the alloy. The addition of nickel, silicon, carbon and oxygen as alloying elements provide desired corrosion resistance and strength.

ZIRCONIUM ALLOY WITH IMPROVED POST-IRRADIATION PROPERTIES

Background of the Invention

This invention relates to alloys for use in light water nuclear reactor (LWR) core structural components and fuel cladding. More particularly, this invention relates to a zirconium alloy for such use which exhibits superior corrosion resistance and mechanical properties after irradiation. Still more particularly, this invention relates to a zirconium alloy with improved corrosion resistance and irradiated ductility by controlling its alloy composition to within particular ranges.

Description of the Prior Art

Zirconium alloys are used in the fuel assembly structural components of nuclear reactors, such as in fuel rod cladding, guide or thimble tubes, grid strips, instrument tubes, and so forth because of their low neutron cross section, good corrosion resistance against high pressure/high temperature steam and water, good mechanical strength, and fabricability. Zirconium alloys, particularly those commonly known as Zircaloy-2 and Zircaloy-4 have been used in light water reactor cores because of their relatively small capture cross

SUBSTITUTE SHEET

section for thermal neutrons. The addition of 0.5 to 2.0 percent by weight niobium and up to 0.25 percent of a third alloying element to these Zirconium alloys for purposes of corrosion resistance in the reactor core is suggested in U.S. Pat. No. 4,649,023 as part of a teaching of producing a microstructure of homogeneously disbursed fine precipitates of less than about 800 angstroms. The third alloying element is a constituent such as iron, chromium, molybdenum, vanadium, copper, nickel and tungsten.

Pellet-clad interaction (PCI) resistance is sought in U.S. Pat. Nos. 4,675,153 and 4,664,831 by use of zirconium-based alloys including "zirconium-2.5 w/o niobium". The latter teaching also refers to "Zr-Nb alloys containing about 1.0 to 3.0 w/o Nb". In these patents, oxygen is present "below about 350 ppm of said alloy".

U.S. Pat. No. 4,648,912 teaches improving high temperature corrosion resistance of an alpha Zirconium alloy body by rapidly scanning the surface of the body with a laser beam. The alloy treated included zirconium-niobium alloys. Thus, it has been found by various investigators in the prior art literature that the addition of niobium to a Zirconium alloy for use in light water reactors will reduce hydrogen uptake from waterside corrosion, stabilize alloying element-irradiation defect complexes, and make the alloy more resistant to annealing

-3-

of irradiation damage. It is also reported by investigators that niobium will enhance work hardenability of irradiated Zircaloy but that an addition of niobium above the 1 percent level will not result in further additional benefit in mechanical properties.

An improved ductile irradiated Zirconium alloy is described in U.S. Pat. No. 4,879,093 issued to an inventor in this application. The alloy has a stabilized microstructure which minimizes loss of alloy ductility required to resist release of fission gases and to handle spent fuel safely. The alloy retains a reasonable corrosion resistance in both pressurized water reactors (PWR) and boiling water reactors (BWR) because of its optimum intermetallic precipitate average particle size. The alloy of the '093 patent is based on an alpha phase zirconium-tin-niobium or alpha phase zirconium-tin-molybdenum alloy having characteristics as shown in Table 1 of that patent with niobium, if present, in a range of from a measurable amount up to 0.6 percent by weight. The molybdenum, if present, is in a range of from a measurable amount up to 0.1 percent by weight. The zirconium-tin system is known as "Zircaloy" and, typically, if Zircaloy-4, for example, would also have 0.18 to 0.24 percent by weight iron, 0.07 to 0.13 percent by weight chromium, oxygen in the range of from 1000 to 1600 ppm, 1.2 to 1.7 percent by weight tin, and the remainder Zirconium.

SUBSTITUTE SHEET

U.S. Pat. No. 4,992,240 discloses another Zirconium alloy containing on a weight basis, 0.4 to 1.2% tin, 0.2 to 0.4% iron, 0.1 to 0.6% chromium, not higher than 0.5% of niobium, and balance zirconium, wherein the
5 sum weight proportions of tin, iron and chromium is in the range of 0.9 to 1.5%. Oxygen, according to Fig. 4 of the '240 patent, is about 1770 ppm to 1840 ppm. Niobium is apparently optional, and silicon is not reported.

Recent trends in the nuclear industry include
10 shifts toward higher coolant temperatures to increase the thermal efficiency and toward higher fuel discharge burnups to increase the fuel utilization. Both the higher coolant temperatures and discharge burnups tend to increase the in-reactor corrosion and hydrogen uptake of
15 the Zirconium alloys. The high levels of neutron fluence and simultaneous hydrogen pickup degrade the ductility of Zirconium alloys. For these more demanding service conditions, it is therefore necessary to improve the corrosion resistance and irradiated ductility of
20 Zirconium alloys.

Accordingly, it is a continuing problem in this art to develop a Zirconium alloy having superior ductility after irradiation; good corrosion resistance, especially independent of processing history; reduced
25 hydrogen absorption by the alloy; and a significant solid solution alloy strength.

It is another continuing general problem in this art to improve the corrosion resistance and irradiated ductility of Zirconium alloys used in fuel assembly structural components in nuclear reactors.

5 Description of the Preferred Embodiments

It is an object of this invention, therefore, to provide a Zirconium alloy with improved corrosion resistance.

10 It is an additional object of this invention to provide a Zirconium alloy with an improved irradiated ductility.

It is still another object of this invention to provide a Zirconium alloy with improved corrosion resistance

15 and irradiated ductility.

It is yet another object of this invention to provide a Zirconium alloy with a predetermined alloy composition for improving corrosion resistance and irradiated ductility.

20 The invention is based upon the theory that ductility after irradiation is improved by selecting the composition of the alloy such that, as far as possible, an addition of the different levels of the alloying element does not result in precipitation of new phases in the microstructure apart from the usual zirconium-iron-chromium precipitates observed in commercial Zircaloy-4.

25 The reasons for selecting specific levels of the

different alloying elements are given below, and the composition of the alloy according to the invention is shown in Table 1.

The alloy of the present invention thus
5 includes tin (Sn) in a range of 0.45 to 0.75 wt.%, wherein 0.6 wt.% is typical. The alloy also has iron (Fe) in a range of 0.4 to 0.53 wt.%, and typically 0.45 wt.%; chromium (Cr) in a range of 0.2 to 0.3 wt.% and typically 0.25 wt.%; niobium (Nb) in a range of from 0.3
10 wt.% to 0.5 wt.% and typically 0.45 wt.%; silicon in a range of 50 to 200 parts per million (ppm) and typically 100 ppm; carbon (C) in a range of 80 to 150 ppm and typically 100 ppm; oxygen (O) in a range of from 1000 to 2000 ppm and typically 1600 ppm; and the balance
15 Zirconium.

TIN (SN)

A decrease in the tin level below the 1.2 percent lower limit in zircaloy-4 improves its corrosion resistance.⁽¹⁾ For this reason, the tin level for the
20 alloy of the invention is selected to be in the range of 0.45 to 0.75 wt.%. However, the trend of the mechanical property data regarding the influence of tin content on the thermal creep of Zirconium alloys at 400°C indicates that a decrease in tin level will degrade the creep
25 resistance of Zirconium alloys.⁽²⁾ The selected range of the tin level of 0.45 to 0.75 wt.% tin is expected to

-7-

provide a combination of good corrosion resistance and good creep resistance for the alloy of the invention and that the addition of niobium and iron as discussed below will improve the mechanical properties of the alloy of the invention.

IRON (Fe)

The corrosion resistance of Zircaloy-2 and iron alloys in both 360°C water and 400°C steam depends on the iron level.⁽³⁾ While best corrosion resistance in 360°C water was observed with 0.45 wt.% iron, the best corrosion resistance in 400°C steam was observed at 0.25 percent iron. In order to achieve good corrosion resistance in both steam and water environments, an intermediate value of 0.4 wt. % to 0.53 wt.% Fe was selected for the new alloy of the invention. Since the results of 360°C water autoclave corrosion tests correlate well with the in-PWR corrosion performance of Zirconium alloys, typically 0.45 wt.% of iron is added to the proposed alloy of the invention.

CHROMIUM (Cr)

Chromium is mainly added to improve the strength and creep resistance of the new alloy. The (Fe+Cr) range up to 0.7 wt.% is useful in improving mechanical properties of the alloy without degradation of the corrosion resistance, according to the recent results

SUBSTITUTE SHEET

of Isobe and Matsuo.⁽⁴⁾ Moreover, for zirconium -in- niobium alloys containing iron and chromium, a iron/chromium ratio of about 1.5 appears to give good corrosion resistance. (4) Thus, the chromium range of 0.2 to 0.3 wt.%, and typically 0.25 wt.%, was selected for the new alloy.

NIOBIUM (Nb)

The addition of niobium in an amount from a measurable mount to 0.5 wt.% and typically 0.45 wt.% is to improve the irradiated ductility of the new alloy,⁽⁵⁾ to improve its corrosion resistance, and to reduce hydrogen absorption.⁽⁵⁾ The amount of niobium is limited to retain a predominantly single phase alpha structure of the alloy for superior corrosion resistance, mechanical properties, and good fabricability. It is known that higher levels of iron can increase the hydrogen uptake of the Zirconium alloys. The addition of 0.45 wt.% niobium is expected to negate the effect of higher iron on the hydrogen absorption characteristics of the proposed alloy.

NICKEL (Ni)

Nickel is added in a range of 0.012 to 0.03 wt.%, and typically 0.02 wt.%, to enhance the high temperature corrosion resistance of the zirconium alloy.

SILICON (Si)

The silicon, in a range of 50 to 200 ppm, and typically at 100 ppm, is added as an alloying element to reduce the hydrogen absorption by the alloy and also to
5 reduce the variation of the corrosion resistance with variations in the processing history of the alloy. (1)

CARBON (C)

Carbon is included in a range of 80 to 150 ppm, and typically at 100 ppm. High levels of carbon, i.e.
10 greater than 200 ppm, degrade the in-PWR corrosion resistance of Zirconium alloys and also increase the irradiation growth rate. Low levels of carbon, i.e. lower than 80 ppm result in parallel plate structure after beta quenching that degrades the fabricability of
15 Zirconium alloys. The selected range for the alloy of the invention of 80 to 150 ppm is expected to result in an alloy with good fabricability, low in-PWR corrosion rate, and low irradiation growth.

OXYGEN (O)

20 Oxygen, in a range of 1000 to 2000 ppm, and typically at 1600 ppm, is added as a solid solution strengthening alloying element.

Thus, the invention of the new alloy described in this specification is expected to achieve good
25 corrosion resistance, irradiated ductility, and reduced

SUBSTITUTE SHEET

hydrogen absorption by its selected composition. The exposure of Zirconium alloys to a water reactor environment results in irradiation damage to the microstructure and hydride precipitation. Both of these factors reduce the ductility and corrosion resistance of the irradiated alloys. The higher levels of alloying elements generally improve the strength and creep resistance of Zirconium alloys with a concurrent degradation of the corrosion resistance. A new Zirconium alloy, according to this invention, with optimum levels of tin, iron, chromium, niobium, nickel, silicon, carbon, and oxygen is proposed that should provide a good combination of mechanical properties and corrosion resistance after irradiation.

BIBLIOGRAPHY

- (1) Eucken C. M., Finden, P.T., Trapp -
Pritsching, S. and Weidinger, H. G., "Influence of
Chemical Composition on Uniform Corrosion of Zirconium
Base Alloys in Autoclave Tests",
5 Zirconium in the Nuclear Industry Eighth International
Symposium, ASTM STP 1023, L.F.P. Van Swam and C. M.
Eucken, Eds.; American Society for Testing and Materials,
Philadelphia, 1989, pp. 113-127.
- (2) McInteer, u. A., Baty, D. L. and Stein, K.
10 O., "The Influence of Tin Content on the Thermal Creep of
Zircaloy-", Zirconium in the Nuclear Industry. Eighth
International symposium, ASTM STP 1023, L.F.P. Van Swam
and C. M. Eucken, Eds.; American Society for Testing and
15 Materials, Philadelphia, 1989 pp. 621-640.
- (3) Scott, D.B., "Notes on the Corrosion
Behavior of Zircaloy-2 with Various Levels of Iron
Content," Zirconium Highlights, WAPD-ZH-24, p. 11,
(1960).
- (4) Isobe, T. and Matsuo, Y., "Development of
20 High Corrosion Resistant Zirconium-base Alloys", Zirconium
in the Nuclear Industry: Ninth International Symposium,
ASTM STP 1132, C.M. Eucken and A.M. Garde, Eds., American
Society for Testing Materials, Philadelphia, 1991, pp.
25 346-367.

SUBSTITUTE SHEET

-12-

(5) Garde, A. M., U.S. Patent No. 4,879,093,
"Ductile Irradiated Zirconium Alloy", issue date November
7, 1989.

SUBSTITUTE SHEET

TABLE 1
Preferred Embodiment
Modified Zirconium Alloy

		<u>Range</u>	<u>Typical</u>
5	Tin, Wt.%	0.45 to 0.75%	0.6%
	Iron, Wt.%	0.4 to 0.53%	0.45%
	Chromium, Wt.%	0.2 to 0.3%	0.25%
	Niobium, Wt.%	0.3 to 0.5%	0.45%
	Nickel, Wt.%	0.012 to 0.03%	0.02%
10	Silicon, ppm	50 to 200 ppm	100 ppm
	Carbon, ppm	80 to 150 ppm	100 ppm
	Oxygen, ppm	1000 to 2000 ppm	1600
	ppm		
	Zirconium	Balance	Balance

IN THE CLAIMS

1 1. A Zirconium alloy for use in light water
2 nuclear core structure elements and fuel cladding, which
3 comprises an alloy composition as follows:
4 4 tin, in a range of 0.45 to 0.75
5 wt.%; iron, in a range of 0.4 to
6 0.53 wt.%; chromium, in a range of
7 0.2 to 0.3 wt.% niobium, in a range
8 of 0.3 to 0.5 wt.%; nickel, in a
9 range of 0.012 to 0.03 wt.%;
10 silicon, in a range of 50 to 200 ppm;
11 carbon, in a range of 80 to 150 ppm;
12 11 oxygen, in a range of 1000 to 2000
13 ppm; and the balance being of
14 zirconium.

1 2. The alloy composition as set forth in
2 claim wherein said tin is typically about 0.6 wt.%.

1 3. The alloy composition as set forth in
2 claim wherein said iron is typically about 0.45 wt.%.

1 4. The alloy as set forth in claim 1 wherein
2 said chromium is about 0.25 wt.%.

1 5. The alloy as set forth in claim 1 wherein
2 said niobium is about 0.45 wt.%.

1 6. The alloy as set forth in claim I, wherein
2 said nickel is about 0.02 wt.%.

1 7. The alloy as set forth in claim 1 wherein
2 said silicon is about 100 ppm.

1 8. The alloy as set forth in claim 1 wherein
2 said carbon is about 100 ppm.

1 9. The alloy as set forth in claim 1 wherein
2 said oxygen is about 1600 ppm.

1 10. A Zirconium alloy for use in light water
2 nuclear core structure elements and fuel cladding, which
3 comprises a composition which includes tin in a range of
4 0.45 to 0.75 wt.% to improve corrosion resistance of said
5 alloy in combination with iron in a range of 0.4 to 0.53
6 wt.% and niobium present in a range of a measurable
7 amount up to 0.5 wt.%, said iron and said niobium acting
8 in combination with said tin to improve the mechanical
9 properties of said alloy, said niobium negating at least
10 in part an increase of hydrogen uptake in said alloy as a
11 result of said iron level; chromium in an amount
12 determined by a ratio of iron/chromium of about 1.5, so

13 that said chromium is in a range of 0.2 to 0.3 wt.%; and
14 alloying elements including nickel in a range of 0.012 to
15 0.03 wt.% to enhance the high temperature corrosion
16 resistance of the alloy, silicon in a range of 50 to 200
17 ppm to reduce the hydrogen absorption by the alloy and to
18 reduce variation of corrosion resistance with variation
19 in the processing history of the alloy, carbon in a range
20 of 80 to 150 ppm for good fabricability, low in-PWR
21 corrosion rate, and low irradiation growth, and oxygen in
22 a range of 1000 to 2000 ppm as a solid solution
23 strengthening alloying element; and the remainder
24 zirconium.

1 11. The alloy composition as set forth in
2 claim 10, wherein said tin is typically about 0.6 wt.%.

1 12. The alloy composition as set forth in
2 claim 11, wherein said iron is typically about 0.45 wt.%.

1 13. The alloy as set forth in claim 11 wherein
2 said chromium is about 0.25 wt.%.

1 14. The alloy as set forth in claim 10 wherein
2 said niobium is about 0.45 wt.%.

1 15. The alloy as set forth in claim 10,
2 wherein said nickel is about 0.02 wt.%

-17-

1 16. The alloy as set forth in claim 10 wherein
2 said silicon is about 100 ppm.

1 17. The alloy as set forth in claim 10 wherein
2 said carbon is about 100 ppm.

1 18. The alloy as set forth in claim 10 wherein
2 said oxygen is about 1600 ppm.

1 19. A Zirconium alloy consisting essentially
2 of the following composition:
3 tin, in a range of 0.45 to 0.75 wt.%;
4 4 iron, in a range of 0.4 to 0.53
5 wt.%; 5 chromium, in a range of 0.2
6 to 0.3 wt.% 6 niobium, in a range of
7 0.3 to 0.5 wt.%; nickel, in a range
8 of 0.012 to 0.03 wt.%; silicon, in a
9 range of 50 to 200 ppm; carbon, in a
10 range of 80 to 150 ppm; oxygen, in a
11 range of 1000 to 2000 ppm; and the
12 balance being of zirconium.

1 20. A Zirconium alloy which comprises a
2 composition consisting essentially of tin in a range of
3 0.45 to 0.75 wt.% to improve corrosion resistance of said
4 alloy in combination with iron in a range of 0.4 to 0.53
5 wt.% and niobium present in a range of a measurable

SUBSTITUTE SHEET

-18-

6 amount up to 0.5 wt.%, said iron and said niobium acting
7 in combination with said tin to improve the mechanical
8 properties of said alloy, said niobium negating at least
9 in part an increase of hydrogen uptake in said alloy as a
10 result of said iron level; chromium in an amount
11 determined by a ratio of iron/chromium of about 1.5, so
12 that said chromium is in a range of 0.2 to 0.3 wt.%; and
13 further comprising alloying elements including nickel in
14 a range of 0.012 to 0.03 wt.% to enhance the high
15 temperature corrosion resistance of the alloy, silicon
16 in a range of 50 to 200 ppm to reduce the hydrogen
17 absorption by the alloy and to reduce variation of
18 corrosion resistance with variation in the processing
19 history of the alloy, carbon in a range of 80 to 150 ppm
20 for good fabricability, low in-PWR corrosion rate, and
21 low irradiation growth, and oxygen in a range of 1000 to
22 2000 ppm as a solid solution strengthening alloying
23 element; and the remainder zirconium.

1 21. The alloy composition as set forth in
2 claim 20, consisting essentially of said alloying
3 elements.

SUBSTITUTE SHEET

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C22C16/00 G21C3/07

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C22C G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 468 093 (COMBUSTION ENGINEERING) 29 January 1992 see the whole document ---	1-21
A	EP,A,0 380 381 (FRAMATOME) 1 August 1990 see the whole document ---	1-21
A	EP,A,0 415 134 (WESTINGHOUSE ELECTRIC CORPORATION) 6 March 1991 *Claims 1-9* -----	1-21

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

5 November 1993

Date of mailing of the international search report

23. 11. 93

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

LIPPENS, M

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No
PCT/US 93/07530

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0468093	29-01-92	US-A- 5080861	14-01-92
		JP-A- 4232220	20-08-92
EP-A-0380381	01-08-90	FR-A- 2642215	27-07-90
		CA-A- 2007872	23-07-90
		CN-A- 1045480	19-09-90
		JP-A- 2271291	06-11-90
		US-A- 5023048	11-06-91
EP-A-0415134	06-03-91	US-A- 5112573	12-05-92
		CA-A- 2024068	01-03-91
		CN-A- 1050225	27-03-91
		JP-A- 3090527	16-04-91
		US-A- 5230758	27-07-93